

# Reductive Coupling Reactions Catalyzed by a Novel Dicobalt Complex

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## 1. Introduction

Vitamin B<sub>12</sub>-dependent enzymes, involving the cobalt species as a reaction site, catalyze various isomerization reactions leading to the intramolecular exchange of a functional group and a hydrogen atom between neighboring carbon atoms. We have been dealing with a hydrophobic vitamin B<sub>12</sub>, which have ester groups in place of the peripheral amide moieties of the naturally occurring vitamin B<sub>12</sub>.<sup>1</sup> The key intermediate in the enzymatic reactions is a compound with Co-C bond. The compound with Co-C bond is quite useful for forming a radical species. The Co-C bond is readily cleaved homolytically by photolysis, electrolysis, and thermolysis to form Co(II) and corresponding radical species. The application of the compound with Co-C bond to organic synthesis is very interesting from the viewpoint of a radical forming reagent.<sup>2</sup> We would like to propose a novel method for dimerization reactions. What's happen when a dicobalt complex with Co-C bonds is irradiated with visible light? Homolysis of Co-C bonds will be done, and the corresponding radical species will form. If the radical parts are close to each other, the two radicals will be coupled each other to form a dimeric compound as shown in Scheme 1. We are dealing with dicobalt complexes with such idea.

## 2. Redox Behavior of a Dicobalt Complex

The redox behavior of a novel dicobalt complex (1) was investigated by means of cyclic voltammetry in THF, and compared with that for the corresponding mononuclear complex (2). Redox pairs of Co(III)Co(III)/Co(II)Co(II), Co(II)Co(II)/Co(II)Co(I) and Co(II)Co(I)/Co(I)Co(I) for the complex 1 were observed at +0.37 V, -1.22 V and -1.41 V vs. Ag/AgCl, respectively. On the other hand, redox pairs identified to Co(III)/Co(II) and Co(II)/Co(I) were observed at +0.52 V and -1.22 V vs. Ag/AgCl, respectively, for the mononuclear complex 2.

## 3. Catalytic Dimerization Reactions

The electrolyses of alkyl halides were carried out in a one-compartment cell equipped with a Pt mesh cathode and a zinc plate anode under an argon atmosphere during irradiation with a 500-W tungsten lamp. The zinc electrode was used as a sacrificial anode. When electrolyses of phenethyl bromide and pentyl bromide were carried out at -1.60 V vs. Ag/AgCl in the presence of the dicobalt complex 1, the dimerization products were predominantly obtained as shown in Eqs. (1) and (2), compared with those for the mononuclear complex 2. A possible reaction mechanism is shown in Fig. 1.

## References

- 1) For example, Y. Hisaeda, *New Challenges in Organic Electrochemistry*, Ed. by T. Osa, Gordon & Breach, 307-321 (1998); Y. Hisaeda, J. Takenaka, Y. Murakami, *Electrochimica Acta*, **42**, 2165 (1997).
- 2) For example, Y. Hisaeda, T. Nishioka, Y. Inoue, K. Asada, T. Hayashi, *Coord. Chem. Rev.*, **198**, 21 (2000); H. Shimakoshi, A. Nakazato, T. Hayashi, Y. Tachi, Y. Naruta, Y. Hisaeda, *J. Electroanal. Chem.*, in press.

Scheme 1

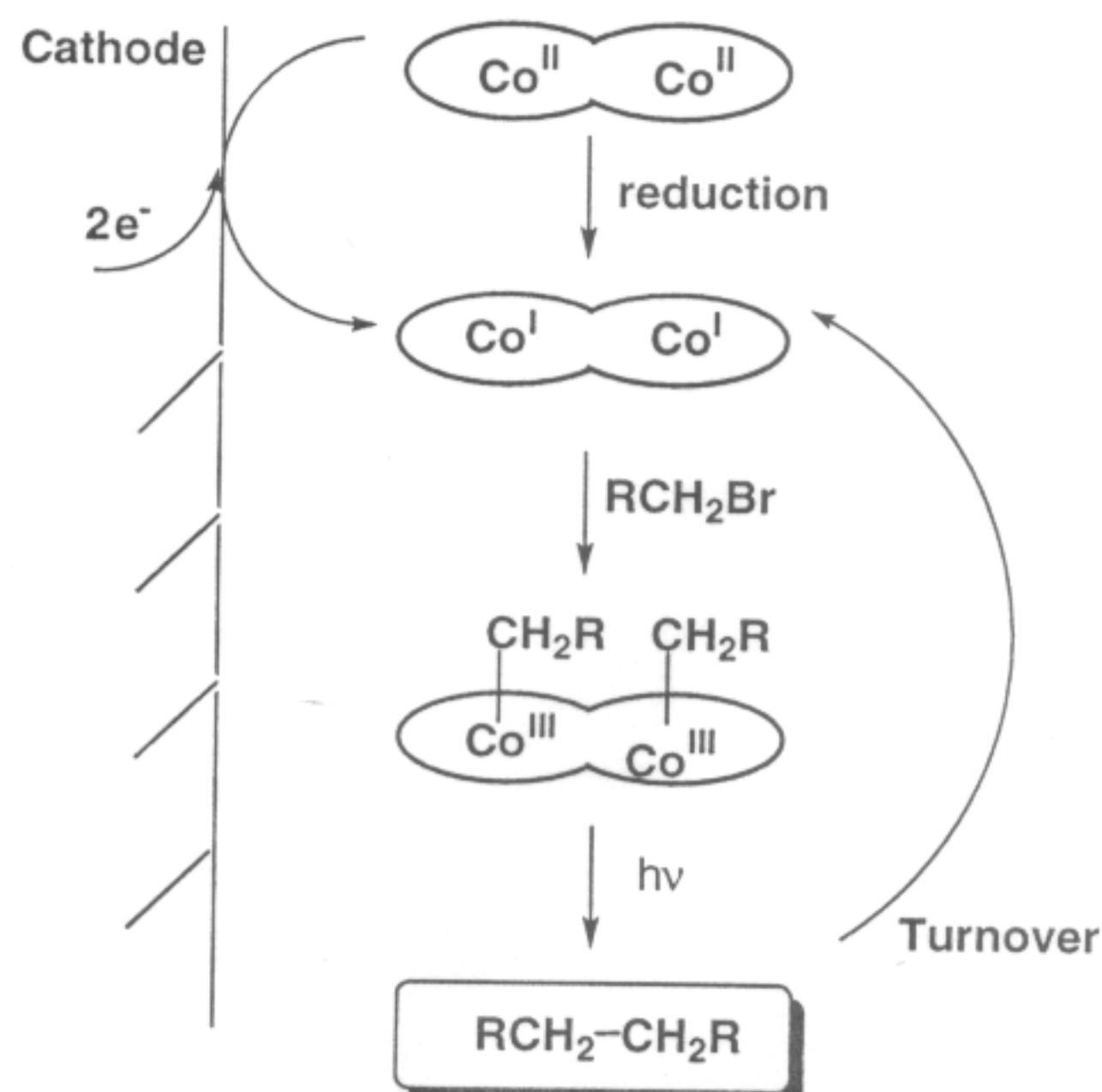
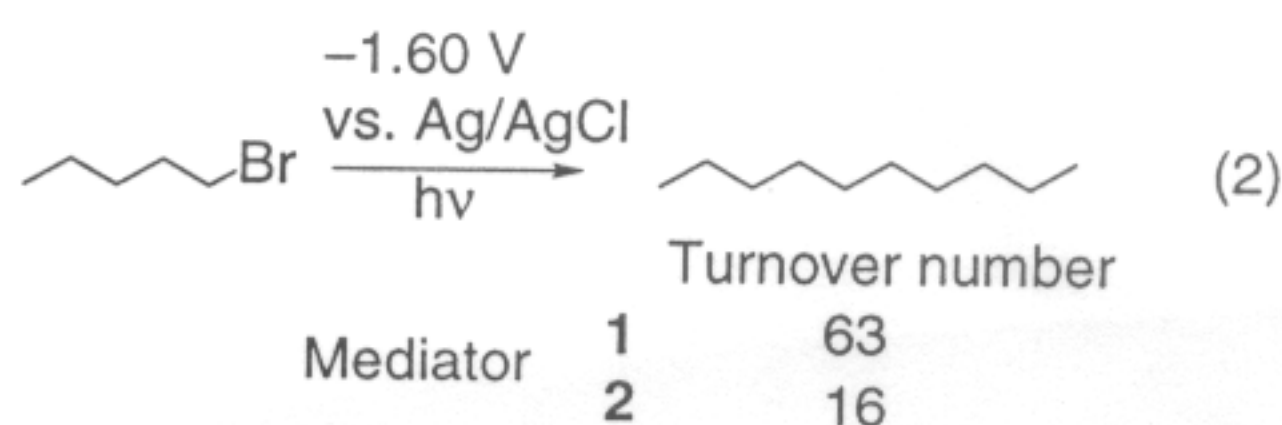
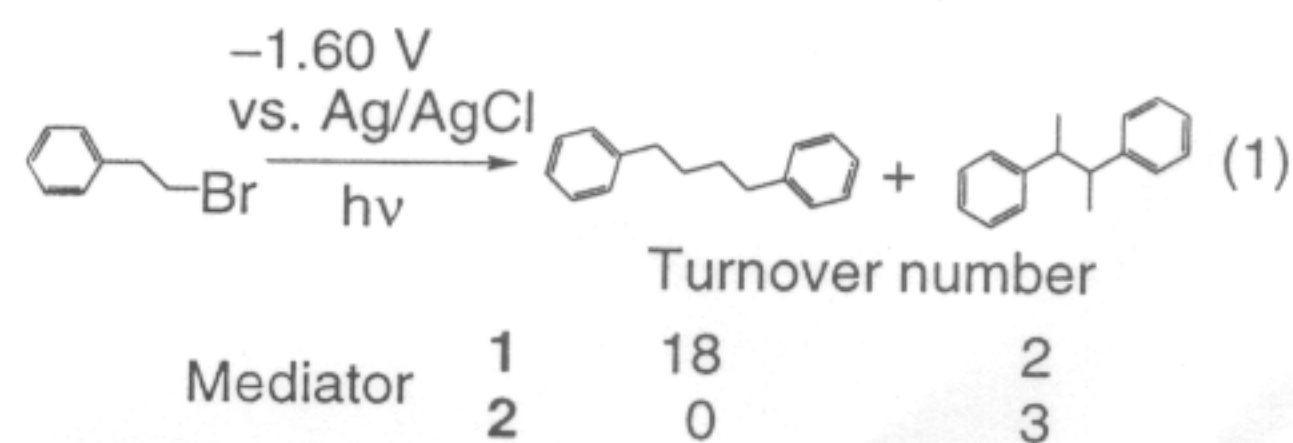
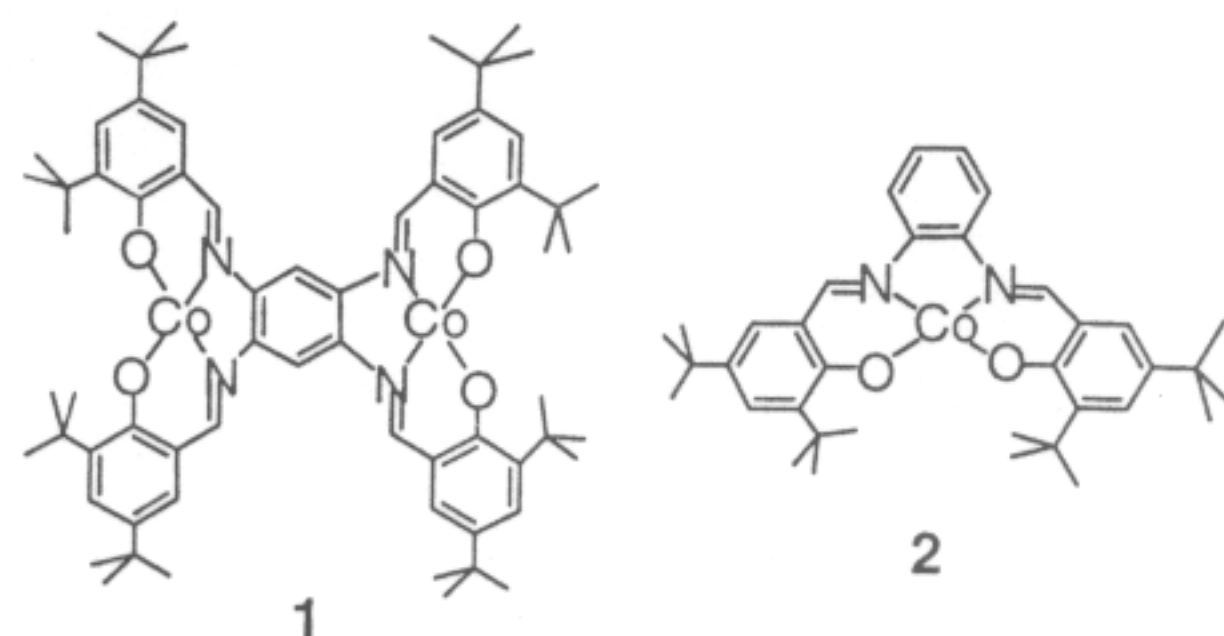
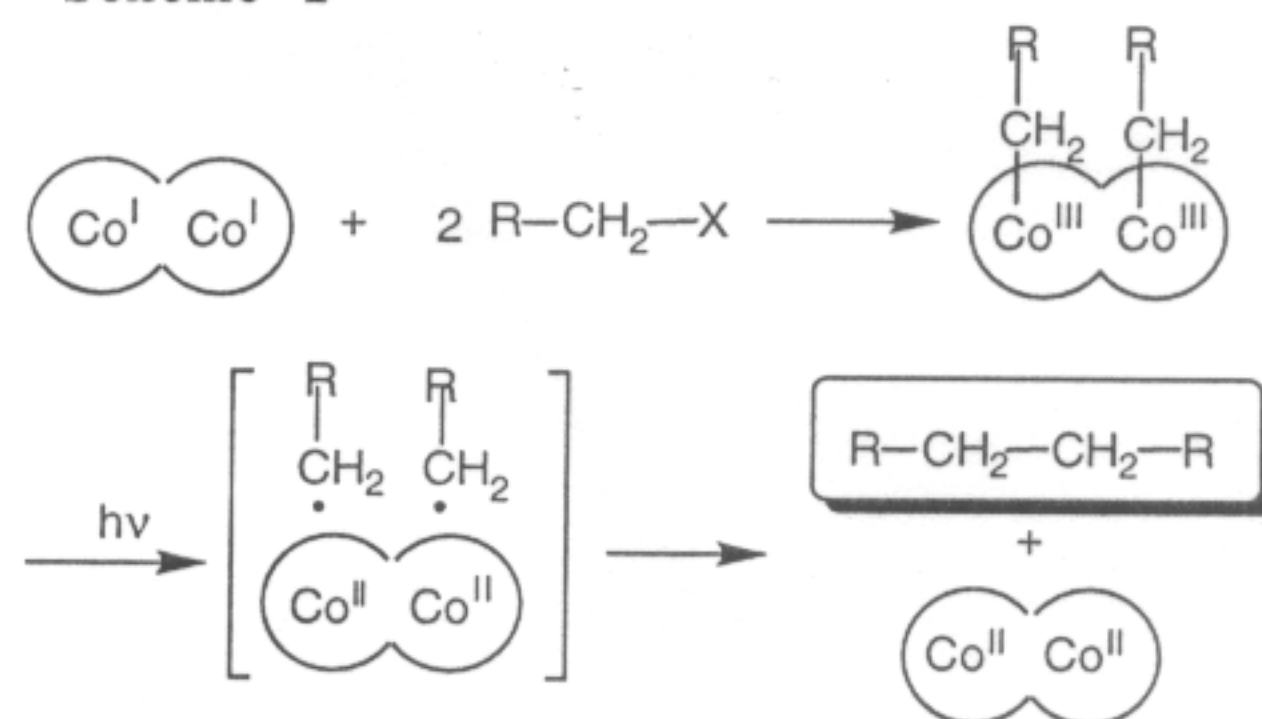


Fig. 1 Proposed mechanism for the electrolysis